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# Radiation resistance of quartz glass for VUV discharge lamps

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## Abstract

Electrically-fused quartz glass, flame-fused quartz glass and plasma-fused quartz glass as well as synthetic fused silica samples were irradiated stepwise with a high energy Xe barrier discharge excimer lamp at 172 nm. VUV spectra were measured before and after every irradiation step. The results show that the VUV transmittance and the resistance against high energy radiation strongly depend on the quartz glass type, as well as on the thermal pretreatment of the quartz glass samples. In electrically-fused and plasma-fused quartz glass the VUV transmission decreases by the formation of oxygen deficiency and E' centres with absorption bands at 163 nm and 215 nm. Best irradiation resistance is found in synthetic fused silica and in thermally treated flame-fused quartz glass.

Photoluminescence spectra measured under excitation with a KrF excimer laser before and after irradiation indicate fundamental differences in the SiO<sub>2</sub> network structure of the different quartz glass types. Whereas a poor radiation resistance correlates with a blue photoluminescence band at 390 nm, the photoluminescence of flame-fused quartz glass changes from blue to green by a thermal treatment which is correlated with a significant improvement of radiation resistance. A simplified model is presented referring to hydride and oxygen deficiency centres as precursors to colour centre formation in different types of quartz glass.

## 1. Introduction

In past years, the use of UV radiation has become a key process in many industrial applications such as lithography, disinfection and sterilization, curing, vapour deposition and surface cleaning. In addition to well-known UV radiation sources such as low and medium pressure mercury lamps, excimer discharge lamps have become increasingly important. They combine a narrow band emission and a high radiation intensity. Some examples of these are Xe lamps (172 nm), KrCl lamps (222 nm), XeBr lamps (282 nm) and XeCl lamps (308 nm). Xe lamps (172 nm), especially, are used in the semiconductor and display industry for surface cleaning, surface treatment and layer deposition.

Efficient lamp operation requires an optimized filling gas mixture and an envelope material with a high transmittance in the VUV spectral range. For the latter, quartz glass or synthetic fused silica is used. For commercial applications

it is essential to operate the lamp without significant output decrease and to guarantee lamp lifetimes of more than one thousand hours. The high energy of 172 nm photons (7.2 eV) is responsible for photo-induced colour centre formation and the generation of internal tensions and bond breakage in the glassy SiO<sub>2</sub> network. Accordingly, there is increasing interest in highly transparent and highly radiation-resistant types of quartz glass and fused silica.

Point defects always exist in real optical glasses as frozen network imperfections or trace element impurities. Years ago, transmission and radiation resistance of quartz glass were limited by trace impurities such as alkali, alkaline earth and others. These impurities may interact electronically with the glassy network when irradiated with intense light or UV light, and form colour centres by changing their electronic states [4, 10]. Methods of purification of raw material became more sophisticated as applications became more demanding. Driven by the telecommunication and

**Table 1.** Intrinsic and technology-related defect and colour centres in quartz glass and fused silica.

Defect		UV absorption	PL
$\equiv\text{Si}-\text{O}-\text{Si}\equiv$	Strained bond		
$\equiv\text{Si}-\text{Si}\equiv$	Oxygen deficiency centre: ODC (I)	163 nm [9]	
$\equiv\text{Si} \cap \text{Si}\equiv$	Oxygen deficiency centre: ODC (II)	$\sim 243$ nm [2, 20]	288 nm [13], $\sim 390$ nm [11]
$\equiv\text{Si}-\text{H}$	Si-H group		
$\equiv\text{Si}-\text{OH}$	Hydroxyl-group	$\approx 160$ nm	
$\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$	Peroxy bridge	330 nm [16]	
H, H <sub>2</sub> , O, O <sub>2</sub>	Interstitial hydrogen and oxygen		
H <sub>2</sub> O	Interstitial water		
$\equiv\text{Si}\bullet$	Three-fold co-ordinated silicon (E')	215 nm [6, 24]	
$\equiv\text{Si}\equiv$	Two-fold co-ordinated silicon	163 nm, 247 nm [18]	474 nm [13]
$\equiv\text{Si}-\text{O}-\text{O}\bullet$	Peroxy radical	245 nm (?), 161 nm (?) [21]	
$\equiv\text{Si}-\text{O}\bullet$	Non-bridging oxygen hole (NBOH)	265 nm, 630 nm [21]	650 nm [12, 21]

**Table 2.** Quartz glass types after Brückner [4], supplemented by type Vc and VIII.

Type	Method of manufacture
I	Electric melting of quartz crystals in a crucible under vacuum
II	H <sub>2</sub> /O <sub>2</sub> flame fusion of crystalline quartz
III	Hydrolysis of SiCl <sub>4</sub> (or other silanes) in a H <sub>2</sub> /O <sub>2</sub> flame, deposition and consolidation in the same step
IIIa	Hydrolysis of SiCl <sub>4</sub> (or other silanes) in H <sub>2</sub> /O <sub>2</sub> flame, deposition of soot particles to form a porous intermediate body, consolidation to full density in a separate step, no dehydration
IIIb	As IIIa with dehydration of intermediate soot body by Cl or F treatment
IV	Oxidation of SiCl <sub>4</sub> in water vapour free plasma flame
Va	Electric melting of pegmatitic quartz grains in Mo or W crucibles under H <sub>2</sub> -containing atmosphere
Vb	As Va but out-gassed in vacuum or in air
Vc	As Va but melted from synthetic quartz grains
VI	Sintering of colloidal SiO <sub>2</sub> glass powder preforms after chloride reaction purification
VII	Sol-gel route of Si-alkoxide, drying and sintering
VIII	Fusion of quartz crystals by using a plasma arc torch

semiconductor industries, synthetic fused silica grades with extremely low impurity content were developed, making quartz glass one of the purest materials known. In synthetic fused silica almost free of trace element impurities, frozen network imperfections and strained bonds become dominant for the optical properties, especially for optical transmittance and the resistance against high energy radiation [7, 8, 19, 20, 23, 25]. To better understand the photo-induced generation of colour centres in quartz glass it is helpful to classify the various defect types.

*Extrinsic defects* are chemical trace impurities such as alkali, any other metal or chemical element. Natural raw materials used for quartz glass fusion are pegmatitic quartz grain with total impurity levels ranging from few to several hundred parts per million (per weight) and natural rock crystals with a typical impurity content of 10–50 ppm. Raw materials with higher purity are cultured crystals (synthetic crystals), synthetic grain made in a sol-gel process and silanes. The latter are used to produce purest synthetic fused silica by flame hydrolysis. Another source of extrinsic impurities is the manufacturing process. In production, tool materials are used in fusion and hot forming processes, e.g. graphite, tungsten and molybdenum. These materials may contain metal impurities which diffuse into the quartz glass at high temperatures.

*Intrinsic defects* are network imperfections, e.g. two-fold and three-fold coordinated silicon atoms, silicon to silicon bonds (oxygen deficiency centres (ODC)), non-bridging oxygen atoms, peroxy radicals, peroxy linkages, interstitial oxygen atoms and interstitial molecular oxygen. Intrinsic defects are always generated as a result of thermal influence

in the production process and exist as equilibrium or frozen-in defects [19].

Additionally, there are *technology-related defects*. In quartz glass that is fused in an atmosphere containing hydrogen, typical defects are hydride (SiH), hydroxyl (OH) and free hydrogen (H<sub>2</sub>). These defects are also present in very pure synthetic fused silica. Other technology-related defects are the halogens, e.g. chlorine and fluorine, which are often used for hydroxyl removal in order to produce dry synthetic fused silica. In dry fused silica, SiCl or SiF, as well as interstitial chlorine and fluorine may be present [19, 26].

Many defects are known to act as optical absorption or colour centres in the UV and VUV spectral range. Examples are the ODC with an absorption band at 163 nm, the E'-centre with an optical absorption at 215 nm and the 265 nm absorption of the non-bridging oxygen hole centre (NBOH). In table 1, important intrinsic and caused defects, and the related VUV absorption bands are listed.

The optical properties of quartz glass, especially in the VUV, strongly depend on the concentration of the different extrinsic and intrinsic colour centres or on defect centres that are precursors to colour centre formation. Since the presence and the concentration of these defect centres are determined by the raw material used and the production process, it is necessary to differentiate between different manufacturing methods [4] (see table 2).

Quartz glass types I, II and VIII can be produced in small batches and are used in the semiconductor, lamp and chemical industries. Types III and IIIa synthetic fused silica contain hydroxyl and are used for applications in UV optics.

**Table 3.** OH and impurity content of samples without thermal treatment.

Sample (type)	OH (ppm)	Impurity content (ppb)								
		Li	Na	K	Mg	Ca	Fe	Cu	Ti	Al
II	156	550	30	<20	20	<30	100	<50	<10	8 230
II*	180	840	520	90	40	710	50	<50	2590	21 000
IIIb	<1	<10	<50	<10	<10	<50	<20	<10	<50	<50
IIIa	201	<10	<50	<10	<10	<50	<20	<10	<50	<50
III	530	<10	<50	<10	<10	<50	<20	<10	<50	<50
III	867	<10	<50	<10	<10	<50	<20	<10	<50	<50
III	1068	<10	<50	<10	<10	<50	<20	<10	<50	<50
Va	110	390	220	220	19	510	70	59	910	14 200
Vc	10	<10	40	40	20	40	80	<50	20	50
VIII	5	1680	50	<20	50	50	130	<50	40	8 020

**Table 4.** Measured concentration of H<sub>2</sub>, OH and SiH of selected samples.

Sample/ type	Thermally treated	Tf (°C)	H <sub>2</sub> (1 cm <sup>-3</sup> )	OH (ppm)	SiH (1 cm <sup>-3</sup> )	$\Delta k_m$ (215 nm) (measured)	$\Delta k_e$ (215 nm) (expected)
III		1091	6.0E+18	530	1.5E+18	1.5	2.8
III	×	996	n.d.	485	n.d.	n.d.	0.0
III		1031	1.4E+18	1068	1.0E+17	0.3	0.2
III	×	979	n.d.	1062	n.d.	n.d.	0.0
II*		1369	2.3E+17	180	2.2E+18	4.4	4.1
II*	×	1144	n.d.	139	n.d.	n.d.	0.0
II		1358	2.8E+17	156	3.3E+18	7.0	6.2
II	×	1130	n.d.	129	n.d.	n.d.	0.0
Va		—	—	110	2.3E+19	See text	42.9
Va	×	1120	—	5	3.0E+18	See text	5.6

OH-free dry synthetic silica (type IIIb) was developed for high IR transmittance in the telecommunications industry. For standard applications in the semiconductor and lamp industries, quartz glass types Va and Vb are used, which can be produced in large batches of several tons.

## 2. Experimental

Different types of quartz glass and synthetic fused silica samples listed in table 3 were chosen for 172 nm irradiation: flame-fused quartz glass made from cultured crystals (II) and rock crystal (II\*), plasma-fused quartz glass made from cultured crystals (VIII), synthetic fused silica types III, IIIa and IIIb made from SiCl<sub>4</sub> or a chlorine-free precursor, as well as type Va and Vc quartz glass made from natural raw material and synthetic quartz grain, respectively [17].

For irradiation experiments, two samples of every material grade were taken from tubes of about 1 mm wall thickness (II, II\*, Va, Vc, VIII) and from plates of 2 mm wall thickness (III, IIIa, IIIb). One sample of each pair was thermally pre-treated at temperatures of about 1000°C for 40 h in vacuum.

Prior to irradiation, all samples were characterized by measuring the VUV transmission from 150 to 240 nm, respectively from 150 to 350 nm (VUVaS 2000 spectrometer, McPherson Inc.), the OH content and the trace impurity content (see table 3). Selected samples were further characterized by measuring the fictive temperature (Tf) as well as the content of molecular hydrogen (H<sub>2</sub>) and hydride (SiH) by Raman spectroscopy using a XY Dilor spectrometer (see table 4). In addition, photoluminescence spectra of the samples were measured. For excitation, a 248 nm excimer laser (LPX 240i, Lambda Physik AG) with a pulse energy density of about 200 mJ cm<sup>-2</sup> was used.

After characterization, the samples were irradiated stepwise for more than one thousand hours with a Xe dielectric barrier discharge lamp (Excimer Lamp 172/330Z, Heraeus Noblelight). The lamp emits incoherent narrow band radiation (band half-width <15 nm) with a band maximum at 7.2 eV (172 nm) [3]. The excimer lamp has a total length of 850 mm and consists of two coaxial arranged tubes with an outer diameter of 30 mm. The inner tube is cooled with de-ionized water. The electrodes are made from a metallic net. One electrode is placed in the inner tube and the other one around the outer tube. The electrical power consumption is 15 W per centimeter lamplength and the operation frequency, about 300 kHz. A detailed description of the physical principles is given elsewhere [5].

For irradiation, samples were placed directly onto the lamp tube. The lamp was operated in a nitrogen atmosphere. The irradiation intensity at the sample position was estimated to be 160 mW cm<sup>-2</sup>, using the electric power input and the power-to-light conversion. The excimer lamp does not emit visible or infrared radiation. Therefore, the samples were irradiated at about room temperature and thermally assisted healing effects do not need to be considered.

## 3. Results

In figure 1 the transmission and photoluminescence spectra of different synthetic fused silica samples with and without thermal treatment after different hours of irradiation are shown. The samples differ in their content of H<sub>2</sub>, SiH and OH. Details of selected samples are listed in tables 3 and 4. All samples with the exception of type IIIb show a good VUV transmission prior to irradiation.

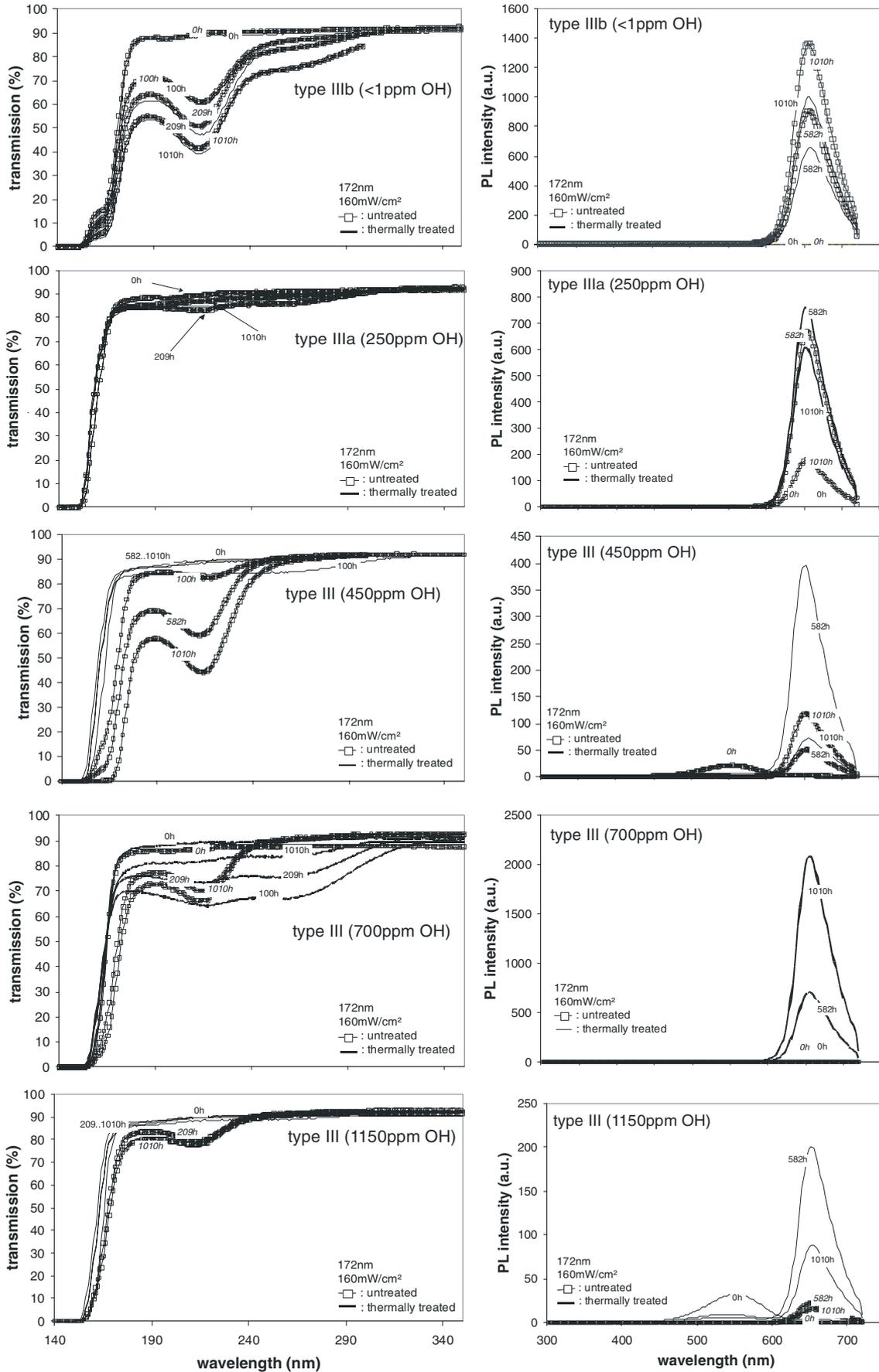


Figure 1. Damage behaviour and photoluminescence of different types of synthetic fused silica.

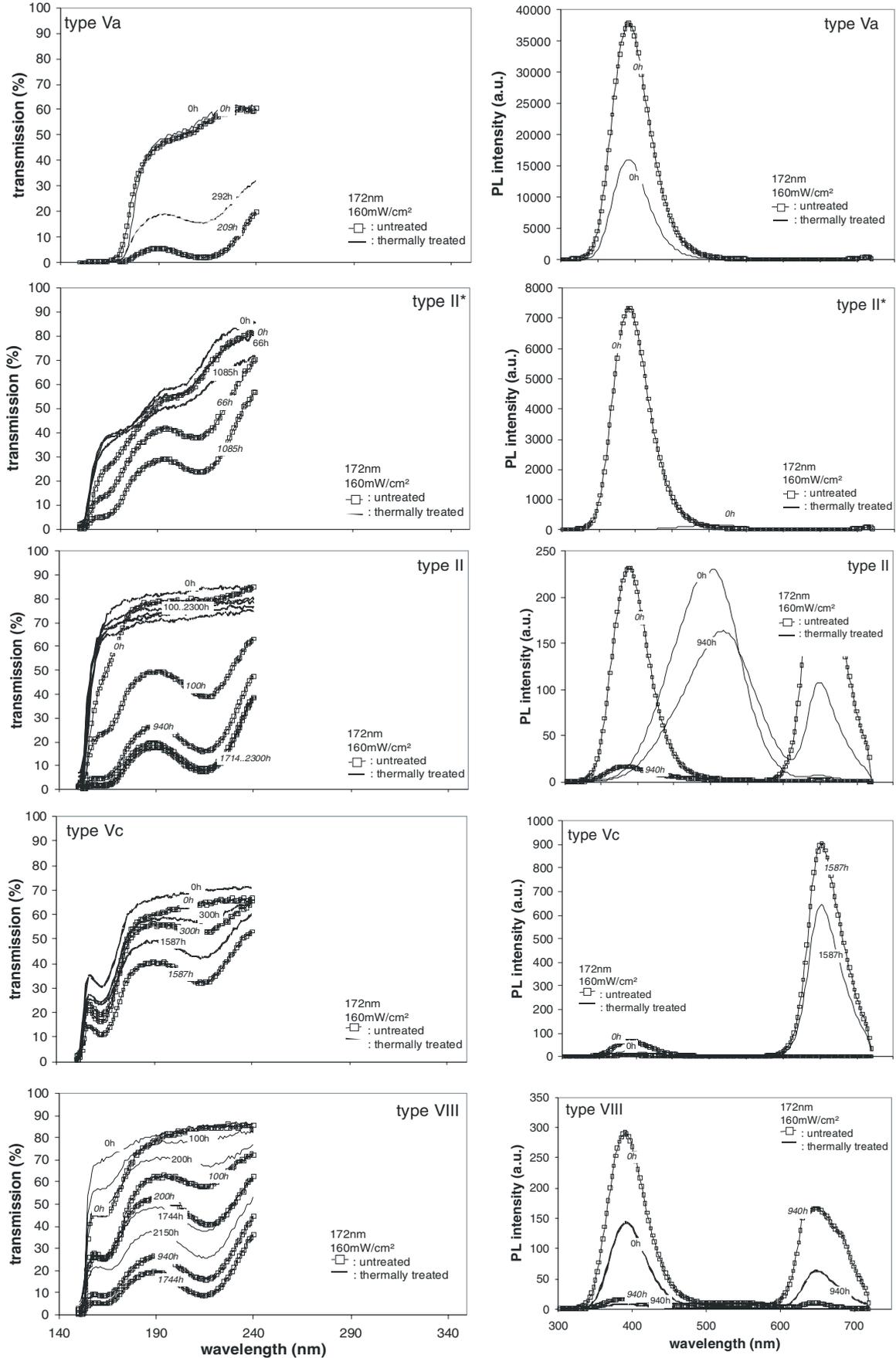


Figure 2. Damage behaviour and photoluminescence of different types of vitreous silica.

The type IIIb sample which has been dried to an OH content of <1 ppm by the use of chlorine shows a strong ODC(I) absorption. Therefore, the absorption edge is shifted to the red [26]. The absorption edge of the other samples is determined mainly by their hydroxyl content. The lower the hydroxyl content, is the better the VUV transmission [15].

There are two groups of synthetic fused silica samples (type III) with a similar radiation damage behaviour: 172 nm irradiation of untreated hydrogen and OH containing samples (type III) produces a strong E' absorption at about 215 nm. The E' absorption saturates with irradiation time. In addition, the generation of an ODC(I) absorption is observed. The absorption strength of the ODC(I) band correlates with that of the E' band. This indicates that both defect types are produced in a similar process. An NBOH absorption is not observed.

In the annealed type III samples, free hydrogen and SiH is not detectable any more (see table 4). In contrast to the not-annealed samples, the formation of E' and ODC(I) is widely suppressed in thermally treated samples. On the other hand, these samples show a more pronounced NBOH absorption at about 265 nm. Another difference in the not-annealed samples is the time-dependent damage behaviour. In not-annealed samples, transmission decreases with increasing irradiation time and may saturate. The longer the irradiation is the stronger the induced absorption at 163 and 215 nm. In contrast to this, annealed samples show a partially inverted behaviour. After about 100 h of irradiation the induced absorption is maximal. Then, with ongoing irradiation, absorption bands become weaker. After about 1000 h of irradiation, absorption bands almost disappeared.

The type IIIa sample is free of hydrogen in the untreated and thermally treated version. Even after one thousand hours of irradiation, the damage is very low. The damage behaviour is comparable to that of thermally treated type III samples since a weak E' and a weak NBOH band can be observed.

The only material with a qualitatively different damage behaviour is the chlorine-treated type IIIb sample. This sample shows strong degeneration primarily owing to E' and NBOH. Also, ODC(I) is slightly increased. The thermal treatment of type IIIb sample does not change its damage behaviour.

All investigated synthetic fused silica samples show a red photoluminescence at about 650 nm after irradiation with 172 nm. The photoluminescence intensity of the thermally treated samples is higher compared with the untreated samples (see graphs on right hand side of figure 1).

Figure 2 shows the experimental results produced by 172 nm irradiation of samples that were made by flame-fusion (type II), electrical-fusion (type Va, Vc) and plasma-fusion (type VIII). Owing to the use of a different VUV spectrometer, the spectral information is available only up to 240 nm. The type Va samples show a very poor VUV transmission. The VUV transmission becomes even worse after a few hundred hours of 172 nm irradiation and is also true for the thermally treated sample. The type Va samples show a very strong blue photoluminescence band at about 390 nm before and after annealing. With ongoing 172 nm irradiation, the photoluminescence decreases.

The flame-fused sample which is made from rock crystal (II\*) shows a medium VUV transmission. 172 nm irradiation produces an ODC(I) and an E' absorption band. The situation

changes if annealed samples are used for irradiation. The annealing increases the transmission in the wavelength range of about 165 nm. In addition, the resistance to 172 nm radiation is improved. The samples made from cultured crystals (II) show a very similar behaviour. Strong damage owing to ODC(I) and E' formation is observed in the not-annealed sample, whereas the annealed sample is slightly improved in transmission and significantly in radiation resistance. The annealed sample (II) shows virtually no radiation damage. Furthermore, annealed samples (II, II\*) show a different photoluminescence behaviour. Before annealing, a blue photoluminescence at about 390 nm is observed. After annealing, the blue fluorescence vanishes almost completely and a green photoluminescence band at about 500 nm appears.

The type Vc sample initially shows an ODC(I) absorption. The transmission can be slightly improved by annealing. Owing to irradiation, E' and ODC(I) bands are induced. Annealing only slightly improves the damage behaviour. The thermally treated and untreated samples show weak photoluminescence at 390 nm and a red photoluminescence band at 650 nm after irradiation.

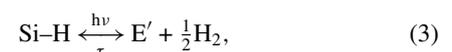
The unannealed type VIII sample shows an ODC(I) absorption which can be almost removed by annealing. Irradiation of all type VIII produces strong E' and ODC(I) absorption bands. Photoluminescence bands can be observed in the blue as well as in the red for the irradiated samples. The blue emission of the unirradiated sample is reduced by annealing. In addition, the 390 nm photoluminescence band in type VIII samples is significantly reduced by 172 nm irradiation. Simultaneously, the red emission band at 650 nm appears.

#### 4. Discussion

The different material types show a wide variation in radiation damage and photoluminescence. It is known that high OH containing synthetic fused silica often has a good radiation resistance. OH groups lower the viscosity of the SiO<sub>2</sub> network and probably reduce the number of strained bonds. Annealing also results in relaxation of network bonds. It is described by Hosono *et al* [8] that strained bonds and physical disorder play an important role in the photolysis of SiO<sub>2</sub>.

However, in a simplified model it is possible to qualitatively describe the observed behaviour with only a few reactions and the potential precursors to defect centres. Some of the latter can be measured well.

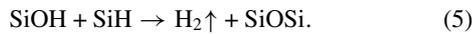
Considering the synthetic samples (type III, IIIa) which show (nearly) no photoluminescence and no defects bands prior to irradiation (see figure 1), extrinsic impurities should not affect the VUV transmission and radiation resistance. The impurities in these samples are intrinsic or technology related, namely SiH, SiOH and H<sub>2</sub> (see table 1). The following reactions [6,22] are possible:



Reaction (1): photoinduced network breakage and creation of NBOH and E' absorption centres. Reaction (2): if molecular hydrogen is available, NBOH centres may be converted to SiOH with a certain relaxation time  $\tau$ . Reaction (3): SiH can be broken up easily to form a E' centre, recombination is possible if molecular hydrogen is still available. Reaction (4): E' centres can form ODC centres or vice versa.

Owing to reactions (3) and (4), all not-annealed SiH and H<sub>2</sub> containing type III samples mainly show E' and ODC formation, but no NBOH which can be converted to hydroxyl (2). The observed simultaneous formation of E' and ODC in unannealed samples is an indication for reaction (4).

After annealing the damage behaviour changes dramatically. For thermal treatment the following reaction has to be considered:



All type III samples feature more SiOH than SiH. Therefore, all SiH centres can recombine via reaction (5) and form molecular hydrogen which diffuses out. This results in a more closed network with some residual SiOH. After annealing, reaction (3) is no longer possible and the only source for generation of new defect centres is given by reaction (1). This is observed qualitatively for the irradiated annealed type III samples by the lower amplitude of the E' absorption, the suppressed ODC(I) band and the appearance of a NBOH band. The occurrence of a photoluminescence at 650 nm supports this model. Red photoluminescence at 650 nm is mainly attributed to NBOH [12, 21], which is stronger in the annealed samples, because NBOH cannot be healed by reaction (2).

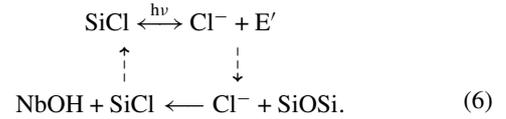
According to the model, the high radiation resistance of the 250 ppm type IIIa sample can be explained by the absence of SiH and molecular hydrogen in both, annealed and not-annealed type IIIa material.

The worse behaviour of the unannealed type III samples (450–1150 ppm OH), therefore, can be attributed mainly to the presence of SiH and the related damage mechanism given by reactions (3) and (4) [17].

A more quantitative description can be given by considering the concentration of intrinsic defects. Table 4 shows the concentration of SiH, H<sub>2</sub> and SiOH of selected samples. Hydrogen and SiH are completely removed from type II and III samples owing to annealing. As expected from reaction (3), the observed E' absorption band at 215 nm should be related to the measured SiH content. For reference, the build-up of the E' absorption and the SiH concentration were measured by 248 nm excimer illumination. From these results the expected change in absorption coefficient  $\Delta k_e$  can be calculated (see table 4). These values correlate well with the measured absorption change  $\Delta k_m$  that can be taken from the transmission spectra. As a rough check for equation (5) the loss of SiOH owing to annealing can be used. Sample type III has an OH content of 530 ppm before, and 485 ppm after, annealing. By taking into account the typical measuring errors this OH loss correlates with the SiH content before annealing, using the following correlation for the OH concentration:  $[1 \text{ cm}^{-3}] = [\text{ppm}] \times 7.8 \times 10^{16}$ .

The chemically dried type IIIb sample contains no molecular hydrogen and no SiH but shows ODC(I) defect centres prior to irradiation. These ODC(I) centres may

be the origin of the E' centre generation during irradiation via reaction (4). However, this material contains chlorine as an additional network modifier (here, approximately 15 000 ppm). It is known from [14] that the Si–Cl bond energy is even less compared with the Si–H which can be broken easily by 172 nm irradiation. Therefore, the following reaction is very likely [1]:



Reaction (6) may lead to E' and NBOH generation and subsequently to additional ODC.

Considering the quartz glass samples shown in figure 2, the type Va shows the worst damage behaviour of all investigated samples. The SiH content is by far the highest for the unannealed samples and the annealed piece still shows the third-highest SiH content of all samples (see table 4). The observed decrease in transmission is far below the expected absorption change,  $\Delta k_e$ . On the other hand, the irradiation of these samples had to be stopped after 280 h owing to the formation of cracks. Therefore, SiH is not completely converted to E' defects in these samples. The poor initial transmission of type Va samples is caused by the high impurity content (see table 3) and ODC(I). The shifting of the transmission edge owing to thermal treatment is remarkable. Because of the very high SiH content, the following reaction for ODC formation is considered:

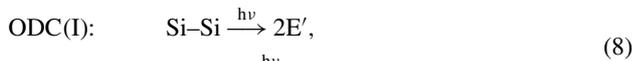


The damage behaviour of samples (II\*, II) made of rock and cultured crystal is very similar. The impurity content of sample II\* is higher for the elements sodium, calcium and titanium (see, table 3) which results in a reduced initial transmission. Regardless of the lower initial transmission, the annealed II\* sample is as stable under VUV irradiation as sample II. Therefore it is concluded that it is not metal impurities but SiH that seems to be the dominant precursor to the damage mechanism. After annealing and complete removal of the SiH, the irradiation resistance of samples II and II\* is significantly increased (compare figure 2 and table 4). The complete disappearance of the ODC(I) absorption and blue photoluminescence in the type II samples after annealing is remarkable. This indicates a relation between ODC and the blue photoluminescence band.

The type Vc and VIII samples both show no SiH even for the unannealed state. The initial transmission can be improved by annealing, but the ODC(I) absorption remains. Both materials show a blue absorption which cannot be removed by annealing. For these sample types, SiH cannot be the precursor to the formation of E' and ODC.

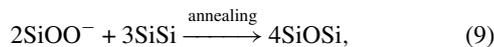
The blue photoluminescence may be associated with the unrelaxed Si–Si bond (ODC(II) defect) that has a very weak optical absorption when compared with the ODC(I) [11]. Owing to the weak absorption, a quantitative determination of the ODC(II) concentration is not possible for the investigated samples. After Imai *et al* [9] the ODC(I) to ODC(II) ratio can be changed by annealing. Therefore, it is proposed that the

ODC(I)  $\leftrightarrow$  ODC(II) transition may be stimulated by VUV irradiation.



Owing to the photoinduced decrease of the observed 390 nm photoluminescence band, this band is attributed to the ODC(II) defect centre. Since ODC(II) is converted to ODC(I) via reaction (8) during irradiation, the amplitude of the blue photoluminescence decreases subsequently. E' may be generated by photoinduced dissociation of ODC(II) or ODC(I). Therefore, all materials with a high initial blue photoluminescence have a poor radiation resistance. The thermally treated type II samples show no blue photoluminescence. This indicates that besides SiH, ODC(II) has been removed from sample II and II\* by thermal treatment. As a result, thermally treated type II samples show an improved radiation resistance. According to Skuja [20], blue photoluminescence at about 390 nm was observed in germanium doped Silica and was associated with GeODC ( $\equiv\text{Ge}\cdot\text{Si}\equiv$ ). On the other hand, sample Vc was fused from the purest synthetic grain but also shows a blue photoluminescence band. From the measured transmission and photoluminescence spectra, it is not possible to differentiate between ODC(II), GeODC or X-ODC, where 'X' stands for any other extrinsic impurity that might play a critical role. For this, additional spectroscopy and decay measurements are necessary. However, from the presented results, the blue photoluminescence can be associated with the precursor to ODC(I) and E'.

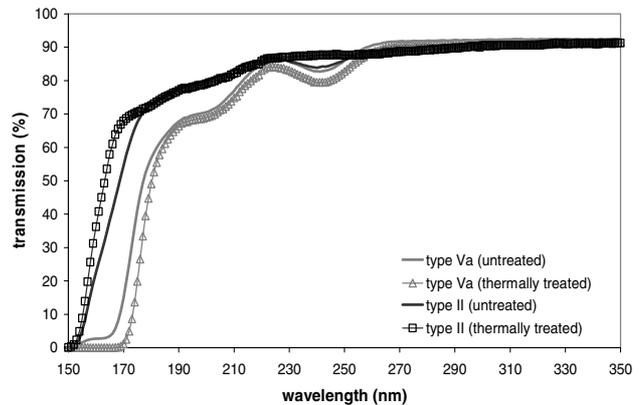
Removal of ODC seems possible only if there are at least, some oxygen surplus areas in the glass. The type II samples feature two absorption centres (ODC at 163 nm and peroxy radical at about 245 nm) which are associated with regions of local oxygen deficit and oxygen surplus, respectively. It is considered that these defect centres recombine during thermal treatment (compare figure 3) to form regular network bonds (9). A second possibility for thermally assisted ODC removal may be the healing of ODC by reaction with interstitial oxygen:



Both processes are not expected in oxygen deficient type Vc and VIII material.

## 5. Conclusion

Radiation damage behaviour of synthetic fused silica (type III, IIIa, IIIb), flame-fused quartz, electrically-fused and plasma-fused quartz glass (types II, Va, Vc, VIII) has been investigated. Strong and rapid solarization owing to the formation of ODC(I) and E' was observed in all samples with a measurable SiH content (i.e. at least  $1 \times 10^{17} \text{ cm}^{-3}$ ). In samples with more SiOH than SiH, the latter can be completely removed by thermal treatment. Therefore, the radiation resistance of these samples is improved significantly. Similar to SiH, SiCl acts as a precursor to ODC(I) and E' generation, but cannot be removed by annealing. ODC(II) also seems to play an important



**Figure 3.** Bleaching of absorption after annealing. In the type II sample the transmission at 163 nm and about 245 nm is improved.

role and is proposed to be a precursor to both, ODC(I) and E' centres. As an indirect measure for the ODC(II) content, the blue photoluminescence with an emission band at 390 nm is proposed. This emission is reduced by 172 nm irradiation and therefore indicates that ODC(II) precursors are converted to ODC(I). The dramatic improvement of radiation resistance of the type II samples made from cultured crystal owing to annealing is remarkable. Damage resistance and initial transmission were both excellent after annealing. Extrinsic impurities do not seem to have a major impact on damage resistance at least for the investigated contamination ranges.

The damage behaviour of the investigated material types and the effect of annealing can be qualitatively explained by only a few of the reactions, which are supported by measurements of material properties or by indirect indicators like photoluminescence.

In conclusion, synthetic fused silica of type IIIa and quartz glass fused from cultured crystals (type II) are identified as best materials for 172 nm VUV applications.

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